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# Determining Binary Diffusion Coefficients for Mixtures in Zeolites from PFG NMR, MD Simulation, and Theory

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## 1. Introduction

Practical applications of zeolites and other nanoporous materials always involve at least two different components, but understanding of multicomponent diffusion in zeolites is limited and experimental data are scarce. The elements of the multicomponent Fickian diffusion tensor for a given system may depend on the total loading of adsorbed molecules, the adsorbed-phase composition, and the temperature. Given the difficulties in measuring multicomponent diffusion coefficients, it would be helpful to have predictive models to calculate the multicomponent diffusion coefficients from single-component data. Several models have been proposed for this purpose. However, given the lack of experimental data, it has been hard to test how widely applicable they are. In this work, we have used atomistic molecular dynamics (MD) simulations to predict binary diffusion coefficients. The results have been used to test the model of Krishna and co-workers [1] for predicting multicomponent behaviour from single-component data. In addition, we report pulsed field gradient (PFG) NMR self-diffusivities for a systematic set of binary mixtures in NaX zeolite.

## 2. Experimental and Simulation Methods

Equilibrium and non-equilibrium MD simulations were performed for mixtures of $CF_4$ and $C_1$ to $C_4$ n-alkanes in a siliceous version of faujasite zeolite. The simulations provided the mixture self-diffusivities, the elements of the Fickian diffusivity matrix, the Onsager coefficients, and the Maxwell-Stefan diffusivities. Details have been reported previously [2].

Self-diffusivities were measured using PFG NMR for binary mixtures of $CF_4$ with n-alkanes, cyclohexane, and benzene in NaX zeolite [3]. Large-crystal NaX samples were provided by G.T. Kokotailo. Measurements were performed on a Varian INOVA spectrometer equipped with an ultra-shielded Doty PFG probe. A short-time diffusion model was used to obtain the unrestricted intra-crystalline self-diffusivity by extrapolating to zero time when no molecules can leave the crystal [4].

## 3. Results

Representative PFG NMR results are shown in Figure 1. Using the Maxwell-Stefan estimation scheme of Krishna, the self-diffusivities in binary systems were estimated from the single-component results. The calculated binary self-diffusivities were consistent with those directly measured in PFG NMR mixture experiments, thus providing an experimental validation of the model. In addition, the effects of mixture composition on the intra-crystalline self-diffusivities were investigated.

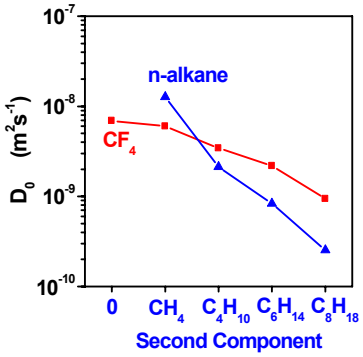


Fig. 1: Self-diffusion coefficients in NaX zeolite loaded with one $CF_4$ (squares) and one n-alkane (triangles) per supercage at 298 K as measured by PFG NMR.

Binary self-diffusivities of methane/$CF_4$, propane/$CF_4$, n-butane/$CF_4$ and n-butane/ethane at various total loadings and mole fractions were also evaluated using MD. In addition, we calculated the Fickian, Onsager, and Maxwell-Stefan diffusivities. As shown in Figure 2, the estimation scheme predicts the binary Onsager coefficients in good agreement with those calculated from non-equilibrium MD.

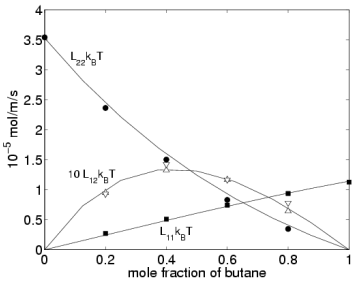


Fig. 2: Onsager coefficients $L_{ij}$ for butane (1) and ethane (2) in faujasite at 300 K and 2.5 total molecules per supercage. Points are from NEMD simulations, and lines are predictions using the model of Krishna [1].

## 4. Conclusion

For the systems studied, the estimation scheme of Krishna and co-workers predicts binary diffusion coefficients in very good agreement with binary data obtained from PFG NMR (self-diffusivities) and NEMD simulations (Fickian, Onsager, and Maxwell-Stefan diffusivities). Future work should focus on testing this and other schemes for other zeolite and adsorbate systems.

## 5. Acknowledgments

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